Preparation of Spherical Submicronic Barium Zirconate particles in Highly Basic Solution below 100°C.

Frédéric Boschini[1*], Rudi Cloots[2] and Bénédicte Vertruyen[2]

[1]APTIS, Departement of Physic, allee du 6 Août, B5a-University of Liège, Belgium
[2]GreenMat-LCIS, Department of Chemistry, University of Liège, Belgium.

* corresponding author: frederic.boschini@ulg.ac.be

Abstract

In this study, a new method has been developed to produce pure crystalline $BaZrO_3$ powders from Ba+Zr solution or weakly soluble reactants by using precipitation route in highly basic aqueous solution. The influence of several synthesis parameters is studied. At high OH^- concentration ([NaOH] = 20 mol/l), it is possible to obtain the well-crystallized stoichiometric perovskite phase at relatively low temperature (~80°C), after a short reaction time (15 minutes) and without requiring any precaution to avoid the presence of CO_2. This synthesis method yields spherical particles, whose size can be controlled by changing the concentration of the Ba+Zr solution. No calcination treatment is necessary since the precipitate is crystalline. Suitable choice of the synthesis parameters ([NaOH] = 20 mol/l, [Ba+Zr] = 1 mol/l, reaction time = 15 minutes) yields a sub-micron precipitate.

1. Introduction

The barium zirconate perovskite is of interest for various fields of applications. $BaZrO_3$ has excellent mechanical properties, such as high fracture toughness, and can be used as refractory up to very high temperatures (T_m = 2600°C). Barium zirconate also shows high corrosion resistance with respect to the molten phases formed during the synthesis of copper oxide–based superconducting single crystals [1] . $BaZrO_3$-$BaTiO_3$ solid solutions are ferroelectric [2] while other $BaZrO_3$-based materials are high-temperature proton conductors [3].
It is well-known that the synthesis of multicationic oxides by classical solid state reaction suffers from several drawbacks, which have stimulated tremendous research into alternative "low temperature" methods. An abundant literature reports successful synthesis routes for a large range of compounds. In the case of $BaZrO_3$, sol-gel oxalate or citrate routes produce powders with very small grain size but many of these methods require organic solvents which have to be recycled [4,5]. It is also possible to synthesise perovskite compounds from aqueous solutions by homogeneous precipitation with urea or ammonia [6,7]. However, most of these syntheses still require a calcination treatment to transform a homogeneous precursor into a crystalline oxide phase.
In this proceeding, we report experimental results on the precipitation of barium zirconate in highly concentrated sodium hydroxide aqueous solution by using [Ba+Zr] solution or weakly soluble powders such as reactants.

2. Experimental procedure

$BaZrO_3$ is prepared by coprecipitation of $BaCl_2.2H_2O$ (99% pure, Mel) and $ZrOCl_2.8H_2O$ (98% pure, Avocado) in a concentrated NaOH (99% pure, J.T Baker) solution or by using pure Ba carbonate and zirconium oxycarbonate powders (99% pure, VWR and 98 % pure,

Alfa Aeser). Solution of cations [Ba+Zr] (0.2, 0.5, 1 mol/l) has added to the pure NaOH solution at a constant flow rate (25 ml/min). Carbonate powders have been added in one time in the hot NaOH solution. The reactor is kept at 80°C during the whole experiment and constant stirring is applied. Powders obtained are then washed with water before characterization.

3. Results and discussion

3.1 $BaZrO_3$ precipitation by using [Ba+Zr] solution

The diffractograms of the powders obtained after precipitation in 20 mol/l correspond to single-phase $BaZrO_3$ perovskite (Fig.1a). The patterns of the powders prepared with 12.5 mol/l or 10 mol/l NaOH reveal the presence of traces of a $BaCO_3$ secondary phase (Fig.1b). The $BaCO_3$ reflections become more intense after storing the powder for several months (Fig.1c). Powders precipitated with 7.5 mol/l NaOH are poorly crystallized (Fig.1d).

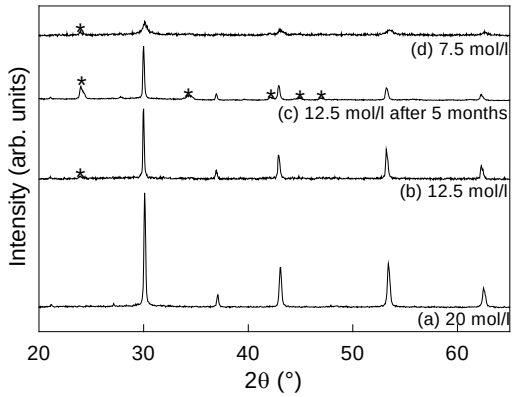

Fig. 1 : Powder X-ray diffraction patterns of the powders precipitated in NaOH solutions of various concentrations. Patterns 1(b) and 1(c) correspond to the same powder and were measured just after the precipitation and after 5 months, respectively. $BaCO_3$ reflections are marked by an asterisk.

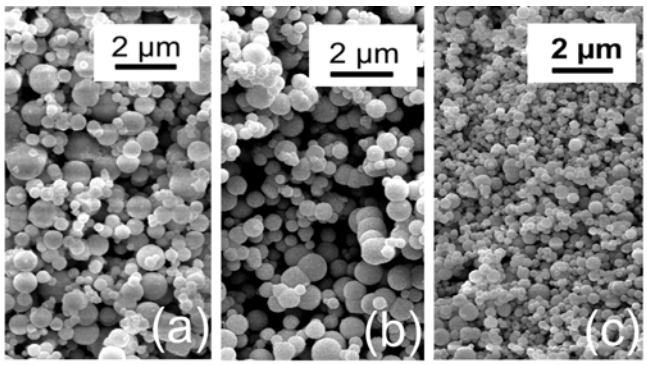

Fig. 2 : Electron micrographs of powders precipitated from solutions with Ba+Zr concentration of (a) 0.2 mol/l, (b) 0.5 mol/l and (c) 1 mol/l. {Other synthesis parameters: [NaOH]=20mol/l, reaction time = 15 min}

ICP-AES analysis was used to measure the barium/zirconium ratio in the precipitates. Powders precipitated in 20 mol/l or 15 mol/l NaOH possess the expected stoichiometry, *i.e.* Ba/Zr = 1. On the contrary, precipitates obtained with lower NaOH concentrations display Ba/Zr < 1. The non-stoichiometry increases when the NaOH concentration decreases (Ba/Zr = 0.89, 0.60 and 0.53 for [NaOH] = 12.5, 10 and 7.5 mol/l), indicating that some barium is left in solution or lost during washing. By comparing the ICP-AES and XRD results, it becomes clear that some Zr-rich amorphous phase must be present in the powders prepared with [NaOH] ≤ 12.5mol/l, since the Zr excess cannot be accommodated as a non-stoichiometry in the $BaZrO_3$ perovskite phase (see [8] for a phase diagram).In summary, pure stoichiometric $BaZrO_3$ is obtained only by precipitation in the most concentrated NaOH solutions (15 or 20 mol/l). The precipitation of the barium zirconate in presence of a large concentration of OH^- can occur through progressive dissolution of the zirconium gel in the solution $ZrO_{1+x}(OH)_{2-2x}$ [9], yielding $Zr(OH)_5^-$ ions which react with the $Ba(OH)^+$ ions [10] (Eq. 1).

$$Ba(OH)^+_{(aq)} + Zr(OH)_5^-{}_{(aq)} \rightarrow BaZrO_{3(s)} + 3\,H_2O \quad \text{(Eq. 1)}$$

When [NaOH] ≤ 12.5mol/l, residual zirconium gel is present in the precipitate. The presence of $BaCO_3$ in these powders results from the adsorption of Ba^{2+} and/or $Ba(OH)^+$ ions on the amorphous zirconia gel or barium zirconate particles. Prolonged exposure of the powder to the air then leads to the formation of $BaCO_3$.
The particle size depends significantly on the [Ba+Zr] concentration. Figure 2 shows the electron micrographs of precipitates obtained after 15 minutes for [Ba+Zr] concentrations of 0.2, 0.5 and 1 mol/l. The particle size decreases when the concentration of reactants increases: addition of a concentrated solution of reactants leads to supersaturation, therefore nucleation is favoured over grain growth [11,12].

3.2 $BaZrO_3$ precipitation by using barium and zirconaium carbonates

The fact that all equilibria are shifted towards the formation of $BaZrO_3$ in the presence of large concentrations of OH^- is further confirmed by the possibility to use weakly soluble reactants. In such an experiment, $BaCO_3$ and oxycarbonate zirconium powders are added directly to the NaOH solution. Figure 3 shows the X-ray diffraction patterns of the powders precipitated in various concentrations of NaOH solutions**.** After adding the powders, stirring for 2 hours, pure $BaZrO_3$ perovskite is obtained for NaOH concentration up to 18 mol./l. This result is in good agreement with the ones obtained before using [Ba+Zr] solution. So, high concentration in NaOH is requested for forming the $Zr(OH)_5^-$ and $Ba(OH)^+$ ions. Figure 4 shows the particles obtained by using carbonates as reactants. The difference in particle size observed between synthesis using [Ba+Zr] solution or as weakly soluble reactants is due to the longer reaction time requiered in the last one. By using weakly soluble reactants, long reaction time allows to Oswald repening process to take place and thus large particles are formed.

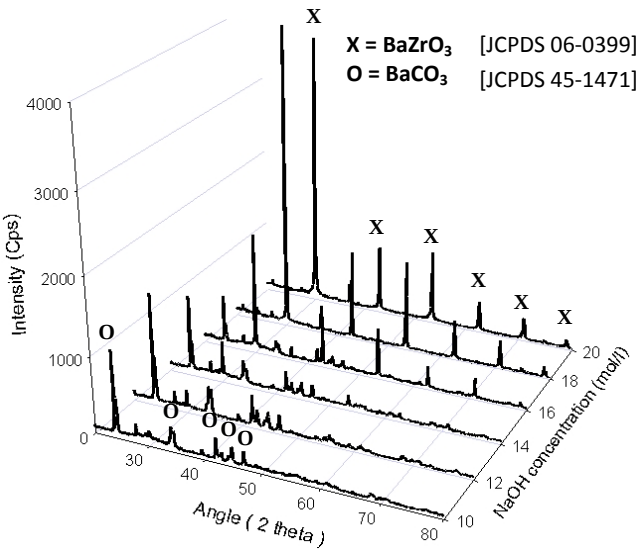

Fig. 3 : Powder X-ray diffraction patterns of the powders precipitated from carbonate powders in NaOH solutions of various concentrations.

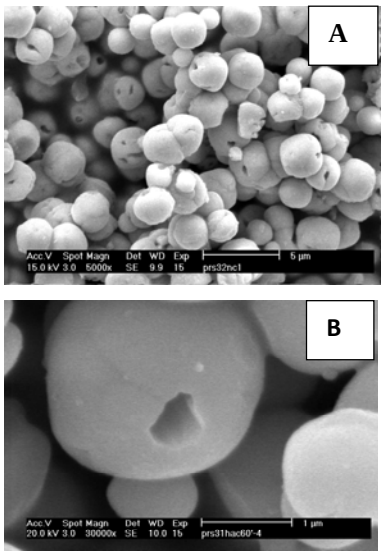

Fig. 4 : Electron micrographs of powders precipitated from scarbonate powders.

4. Conclusions

Pure crystalline $BaZrO_3$ powders can be produced by precipitation in highly basic aqueous solution from [Ba + Zr] solution or weakly soluble reactants. The high OH^- concentration

([NaOH] = 20 mol/l) makes it possible to obtain the well-crystallized stoichiometric perovskite phase at relatively low temperature (~80°C) without requiring any precaution to avoid the presence of CO_2. This synthesis method yields spherical particles whose size can be controlled by changing the concentration of the Ba+Zr solution. No calcination treatment is necessary since the precipitate is crystalline, therefore aggregation of the particles by partial sintering is avoided. Suitable choice of the synthesis parameters ([NaOH] = 20 mol/l, [Ba+Zr] = 1 mol/l, reaction time = 15 minutes). The primary particle size is around 150 nm and the median grain size of the agglomerates is around 900 nm, thus no grinding step is necessary.

5. Acknowledgements

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